

REPORT DOCUMENTATION PAGE		<i>Form Approved</i> OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.			
1. REPORT DATE (DD-MM-YYYY) 29/11/2012	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 31/8/2009 - 31/8/2012	
4. TITLE AND SUBTITLE: Chemical Defects, Electronic Structure, and transport in n-type and p-type organic semiconductors: First principles theory		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER FA9550-09-1-0436	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Dr. John E. Northrup		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304.		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research Dr. Charles Lee 875 North Randolph Street Suite 325, Room 3112, Arlington VA, 22203		10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-OSR-VA-TR-2012-1233	
12. DISTRIBUTION / AVAILABILITY STATEMENT . Approved for Public Release. Distribution is unlimited.			
13. SUPPLEMENTARY NOTES			
14. ABSTRACT This research provided insight into the factors which limit charge mobility in organic semiconductors by performing theoretical studies of electronic structure and defect stability in n-type and p-type semiconductors. In this research we also investigated chemical defects resulting from x-ray irradiation. A description of the research accomplishments is provided in the pages below, as well as in the archival publications supported by this grant.			
15. SUBJECT TERMS organic semiconductors, mobility, defects, electronic structure, radiation induced defects			
16. SECURITY CLASSIFICATION OF:		17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
			19a. NAME OF RESPONSIBLE PERSON John E. Northrup

a. REPORT A	b. ABSTRACT A	c. THIS PAGE A		22	19b. TELEPHONE NUMBER <i>(include area code)</i> 650-812-4117
-----------------------	-------------------------	--------------------------	--	----	--

Final report 8/31/2009 – 8/31/2012

Grant No. FA9550-09-1-0436

**Chemical defects, electronic structure, and transport in n-type and p-type
organic semiconductors: First principles theory**

PI – Dr. John E. Northrup

Palo Alto Research Center

3333 Coyote Hill Road

Palo Alto, CA 94304

650-812-4117

Northrup@parc.com

Program Manager: Dr. Charles Lee

Charles.Lee@afosr.af.mil

703-696-7779

The accomplishments and archival publications are discussed below.

Changes in research objectives: None.

Changes in AFOSR program manager: None.

Extensions granted or milestones slipped: None.

Include any new discoveries, inventions, or patent disclosures during this reporting period: None.

Approved for Public Release. Distribution is unlimited.

Introduction: One of the goals of this research is to determine the mechanisms which limit charge transport in organic semiconductors. Based on observations for single crystals and estimates obtained with theoretical models it seems likely that the upper limit on mobility of organic materials is at least one order of magnitude higher than what is commonly achieved ($1 \text{ cm}^2/\text{Vs}$) in vapor deposited or solution processed devices. It is expected therefore that mobility in solution processed organic semiconductors can be improved significantly by a reduction in the structural disorder, increase in purity, optimization of the semiconductor/gate-dielectric interface, and further improvements in the design of materials. One mechanism limiting the mobility is the presence of grain boundaries. Our work, in collaboration with Stanford and Northwestern, provides insight into the role of grain boundaries in the n-type semiconductor perylene-diimide and will be discussed below. Another mechanism limiting the mobility is the presence of band tail states which may arise from structural order within the grains. Our work for P3HT and PBTTT relates the disorder in the pi-pi stacking distance to the energy breadth of the tail of localized states extending into the gap. We also introduced a simple model allowing estimates of the *upper limit* of the intra-grain mobility in organic semiconductors. The model, discussed below, was applied to the very promising solution processable small molecules DNNT-C₁₀ and BTBT-C₁₂, as well as to pentacene, and DATT. This research will be described below.

In addition to our work on the electronic structure and charge mobility, we have also carried out work on radiation induced defect formation. A deeper understanding of radiation induced degradation mechanisms in organic semiconductors is needed to guide the selection or synthesis of materials with enhanced stability for solar cells and transistors. Theoretical studies can provide valuable information that connects experimental results to specific degradation mechanisms. Recent experimental and theoretical work at PARC provided evidence that x-ray irradiation of polymer/PCBM solar cells abstracts hydrogen from the alkyl-chains with re-attachment of the hydrogen to carbon atoms in the conjugated chains. First-principles calculations show that two types of defects created in this process, hydrogen vacancies in the alkyl chain and CH₂ defects on the conjugated chain, can give rise to states in the energy gap which can trap carriers. The work points to a model in which defect creation caused by radiation induced hydrogen abstraction and defect annealing mediated by hydrogen migration plays a fundamental role.

Discussion of accomplishments published in archival publications

Large modulation of carrier transport by grain-boundary molecular packing and microstructure in organic semiconductors

A collaborative effort involving John Northrup at the Palo Alto Research Center, experimentalists at Stanford (A. Salleo *et al*), and synthetic chemists at Northwestern (T. Marks *et al*) led to a better understanding of the role of grain boundaries. A paper describing the work was published in Nature Materials. {J. Rivnay, L.H. Jimison, J. E. Northrup, M. F. Toney, R. Noriega, S. Lu, T. J. Marks, A. Facchetti, and A. Salleo, *Large modulation of carrier transport by grain-boundary molecular packing and microstructure in organic semiconductors*, Nature Materials **8**, 952 (2009).} The material investigated is the high performance n-type perylene-diimide semiconductor, PDI8-CN₂. We were able to show that grain boundary orientation modulates the mobility by almost two orders of magnitude. By controlling the crystallization direction, determining the molecular packing with respect to the crystallization direction, and measuring the mobility in devices in which the charge transport is either parallel or perpendicular to the crystallization direction, it was discovered that the mobility in this system is determined completely by the characteristics of the grain boundaries that must be traversed by the carriers. In the devices exhibiting the lower mobility, the electrons are required to traverse high-angle grain boundaries separating domains. In the devices exhibiting higher mobility the carriers traverse low-angle grain boundaries. At PARC, first-principles calculations of the molecular packing and surface energies were employed to determine the orientation of the material with respect to the crystallization direction. Surface orientations having low energy were matched with directions along which cracks appeared in some films. Electronic structure calculations performed for PDI8-CN₂ demonstrated that the observed high level of anisotropy did not arise from intrinsic anisotropy of the mobility within a grain. This work shows that control of grain boundary *orientation* in devices may be a fruitful approach to improving performance.

Structural origin of gap states in semicrystalline polymers and the implications for charge transport

Photoconductivity measurements of the electronic structure of organic solar cells

We have shown in calculations for PBTTT and P3HT that disorder in the π -stacking distance gives rise to a tail of localized states which act as traps for electrons and holes. We introduced a simple effective Hamiltonian model to describe the disorder measured experimentally. The matrix elements needed for the model were determined from first principles calculations. The calculations are important because they provide physical justification for the mobility edge (ME) model of transport in polymer semiconductors. The ME model hypothesized that states with energies above a certain energy, the mobility edge, act as localized traps and do not contribute to the mobility, while states with energies below the mobility edge are extended and do contribute to the mobility. {The mobility edge model has been discussed by R. A. Street, J. E. Northrup and A. Salleo, Phys. Rev. B **71**, 165202 (2005).}

In our calculations we find that the localized states in the valence band tail can be characterized by an exponential distribution,

$$N(E) = N_0 \exp[-(E-E_{\text{vbm}})/E_0].$$

E is the energy of the state and E_{vbm} is the energy of the valence band maximum in perfectly ordered regions. The energy E_0 is a measure of the extent of the distribution of localized states, and is found to be ~ 90 meV for the order parameter determined in x-ray scattering experiments. This result is in agreement with experimental measurements which have shown an exponential distribution of band tail states with a similar value of E_0 . Calculations of the wave-functions demonstrate that states having energy $E < E_{\text{vbm}}$ extended while states with $E > E_{\text{vbm}}$ are localized on just a few polymer chains. These calculations therefore provide physical justification for the mobility edge model of transport in polymer semiconductors. These calculations are reported in two papers. Rivnay *et al* presented calculations of the band tail state distribution for PBTTT and structural disorder data obtained by x-ray diffraction for PBTTT.[1] Street, Song, Northrup, and Cowan discussed calculations of the band tail state distribution for P3HT and the effect of band tail states on solar cells.[2,3] The method for calculating the distribution of band tail states was presented by J. Northrup in an invited talk at CECAM-2011 in Lausanne, Switzerland.[4]

- [1] J. Rivnay, R. Noriega, J. E. Northrup, R. J. Kline, M. F. Toney, and A. Salleo, *Structural origin of gap states in semicrystalline polymers and the implications for charge transport*, Phys. Rev. B **83**, 121306 (2011).
- [2] R. A. Street, K. W. Song, J. E. Northrup and S. Cowan, *Photoconductivity measurements of the electronic structure of organic solar cells*, Physical Review B **83**, 165207 (2011).
- [3] R. A. Street, J. E. Northrup, *Density of electronic states model for organic solar cells*. Spring MRS Meeting. San Francisco, CA. April 27, 2011.
- [4] J.E. Northrup, *Sources of gap states and structural disorder in organic semiconductors*. CECAM-2011 February, 2011 Lausanne, Switzerland.

Two-dimensional deformation potential model of mobility in small molecule organic semiconductors

We introduced a model [1] allowing estimates of the upper limit of mobility for organic semiconductors. The model is appropriate for materials where the transport takes place in two-dimensions, such as in the very promising layered materials DNTT-C₁₀ and BTBT-C₁₂. The model is based on the assumption of band transport, which experiments suggest is appropriate for these materials. The model was applied to three materials: DNTT-C₁₀, BTBT-C₁₂, and pentacene. The physical quantities entering the model were obtained by performing first-principles calculations. The model predicts that the mobility of crystalline BTBT-C₁₂ can be as large as 50 cm²/Vs along the fast transport direction and 40 cm²/Vs along the slow direction. According to the model the better mobility in DNTT and BTBT in comparison to pentacene results from smaller effective masses in DNTT and BTBT. Subsequent to this calculation Minemawari *et al.* [2] reported that transistors employing the semiconductor BTBT-C₈ and fabricated with by inkjet printing exhibited hole mobility averaging around 16 and extending up to 31 cm²/Vs. Our independent theoretical results support these measurements. These results show that organic semiconductors fabricated using inkjet printing can be highly ordered and have excellent transport properties. The introduction of this model is also significant because it provides an alternative approach (to the Markus theory) for estimating carrier mobility in high performance organic semiconductors.

A complete description of the new model and its application to these materials was written and published.[1] The structure of these molecules is indicated in Fig. 1. BTBT-C₁₂ and DNTT-C₁₀ consist of two-dimensional layers of

herringbone-stacked molecules.[3,4] The layers are separated from neighboring layers by long alkyl chains, so transport occurs predominantly in two-dimensions. Therefore a 2D acoustic deformation potential model was employed to calculate the mobility for transport within the plane. The model is defined in Figure 2. This is the first time such an approach has been applied to organic semiconductors.[1,5] In this model the mobility depends on the direction of transport and is inversely proportional to the effective mass. In directions for which the effective mass is low the mobility will be high. Our first-principles density functional calculations indicate that the effective masses of BTBT and DNTT are significantly less than values obtained for other organic materials such as pentacene. The effective mass depends on the direction of transport, so the mobility depends on the direction of transport. The directional dependence of the effective mass was calculated and shown in Figure 3. The table shown in Figure 4 shows the results for DNTT-C10, BTBT-C12 and pentacene. The model predicts that the maximum mobility achievable in DNTT is higher than in pentacene.

According to the model the mobility increases linearly with L_{eff} , an effective length that depends on the degree of carrier confinement in the direction perpendicular to the plane of transport. For materials such as DNTT and BTBT, L_{eff} is equal to the length of the π -bonded molecular core. Since the mobility increases as L_{eff} increases, the length of the π -bonded molecular core is identified as an important structural feature affecting mobility in two-dimensional organic semiconductors. *This suggests an avenue to explore in designing materials having superior mobility: increasing the width in the direction perpendicular to plane of transport could be a very effective approach for increasing the mobility of organic semiconductors.*

References:

- [1] J. E. Northrup, *Two-dimensional deformation potential model of mobility in small molecule organic semiconductors*, Applied Physics Letters **99**, 062111 (2011).
- [2] H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas, R. Chiba, R. Kumai, and T. Hasegawa, *Inkjet printing of single-crystal films*, Nature **475**, 364 (2011).
- [3] DNTT-C₁₀ is 2,9-dialkyl-dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene.
- [4] BTBT-C₁₂ is 2,7-dialkyl[1]benzo-thieno[3,2-b][1]benzothiophene.
- [5] J. E. Northrup, *Two-dimensional deformation potential model of mobility in alkylated small molecules: DNTT-C10 and BTBT-C12*, oral presentation at MRS 2012 Meeting, Boston, MA.

Structure and sources of disorder in poly(3-hexylthiophene) crystals investigated by density functional calculations with van der Waals interactions

In other research activity we investigated the structure and sources of disorder in poly(3-hexylthiophene) crystals by performing density functional calculations that included van der Waals interactions. This work was published in Physical Review B **83**, 184117 (2011). [1] In this paper we introduced a new kind of defect which gives rise to disorder in the π -stacking direction. Regio-regular polymers such as P3HT exhibit a directionality along the backbone: the side chains may be attached on the left sides of the thiophenes or on the right sides of the thiophenes. Such left-running or right-running molecules are equivalent, of course, because we can convert one into the other by a simple rotation. (see Figure 5.) However, when the polymer chains aggregate there may arise a *defect* in which a left-running chain is present in a crystallite consisting primarily of right-running chains. Such a defect is illustrated in Figure 5. Our calculations predict that the lowest energy stacking is *all left-running* (or equivalently *all right-running*) chains rather than a mixture of the two

possibilities. Nevertheless it seems likely that in the aggregation process some mistakes will occur and the crystallite will contain some stacking defects. Our calculations indicate that such a defect would cost very little energy. Such defects would *not* occur in molecules such as PBTTT, which do not exhibit this type of directionality. In addition it should be noted that a P3HT polymer that fold back on itself will exhibit this type of stacking. This work presented by J.E. Northrup in an invited talk at the EPFL in Lausanne, Switzerland. [2]

References:

- [1] Weiyu Xie, Y. Y. Sun, S. B. Zhang, and J. E. Northrup, *Structure and sources of disorder in poly(3-hexylthiophene) crystals investigated by density functional calculations with van der Waals interactions*, Phys. Rev. B **83**, 184117 (2011).
- [2] J.E. Northrup, *Sources of gap states and structural disorder in organic semiconductors*. CECAM-2011 February, 2011 Lausanne, Switzerland.

Radiation induced recombination centers in organic solar cells

A deeper understanding of radiation induced degradation mechanisms in organic semiconductors is needed to guide the selection or synthesis of materials with enhanced stability for solar cells and transistors. Theoretical studies can provide valuable information that connects experimental results to specific degradation mechanisms. Recent experimental and theoretical work at PARC provided evidence that x-ray irradiation of polymer/PCBM solar cells abstracts hydrogen from the alkyl-chains with re-attachment of the hydrogen to carbon atoms in the conjugated chains.[1,2,3] First-principles calculations show that two types of defects created in this process, hydrogen vacancies in the alkyl chain and CH₂ defects on the conjugated chain, can give rise to states in the energy gap which can trap carriers. The work points to a model in which defect creation caused by radiation induced hydrogen abstraction and defect annealing mediated by hydrogen migration plays a fundamental role.

Experiments performed by R. Street and at PARC revealed that prolonged x-ray exposure of bulk heterojunction organic solar cells induces deep trap states. These states are observed in measurements of the photocurrent spectral response. The density of induced trap states is proportional to the density of recombination centers as measured by the voltage dependence of the photocurrent, therefore identifying the traps as primary recombination centers. The states are reversible by thermal annealing at about 100 degrees C, which implies a metastable structural change. The activation energy for the thermal annealing is in the range from 1-1.2 eV. From an analysis of the radiation damage it seems likely that defects are formed by hydrogen released from C-H bonds due to interaction with energetic secondary electron-hole pairs. Theoretical structure calculations of possible hydrogen related defects find specific defect states that appear to be consistent with the observations, and provide values for hydrogen migration energies. The effects of prolonged white light exposure are very similar to x-ray exposure, although the annealing properties are significantly different. Measurements of the spectral response with bias illumination provide further insight into the properties of the localized states.

The radiation damage analysis suggests that the trap states are a result of hydrogen release from C-H bonds. First principles density functional pseudopotential calculations were therefore performed to determine the electronic properties and energetics of hydrogen related defects in poly-3-alkylthiophene (P3AT). In particular we examine defects which may be created by transferring H atoms from alkyl-chains to the conjugated polymer backbone. Atomic structure and total energy calculations were performed within the local density functional theory as discussed in previous

calculations for thiophenes, polythiophenes, and pentacene. A plane wave basis is employed with a cutoff energy of 40 Ry. Calculations were performed for both isolated polymers and bulk systems. The length of the repeating unit along the polymer backbone was varied between 4 and 8 S atoms.

A possible explanation for the origin of the gap states in irradiated P3HT involves defects created by breaking a C-H bond in the alkyl-chain or on the thiophene rings, and adding the removed H atom to a C atom in the conjugated backbone. Approximately 4-5 eV is required to break a C-H bond. It is therefore likely that irradiation by x-rays may break C-H bonds in the alkyl chain region of an organic material. This would result in the creation of a free radical defect in which a C atom in the alkyl-chain which was previously four-fold coordinated now has two C-C bonds and one C-H bond. We refer to such a defect as a hydrogen vacancy V_H . Atomic relaxation will occur so that the C atom becomes sp^2 coordinated with a singly occupied 2p orbital. The structure of a V_H defect is illustrated in Fig. 6. H atoms freed by the irradiation may attach to a C atom in the conjugated chain, thereby giving rise to over-coordinated C atoms. One such defect, a CH_2 defect, is shown in Fig. 7.

The preferred location for a hydrogen vacancy in the alkyl chain was determined by calculating total energies for V_H on each of the sites on the alkyl chain as shown in Fig 6. These calculations predict that the V_H prefers to reside on the carbon atom that is nearest to the conjugated chain. Referring to nomenclature defined in Fig. 6 we find $V_H(A1)$ is lower in energy than $V_H(A2)$, $V_H(A3)$, and $V_H(A4)$ by 0.9 eV. This preference for $V_H(A1)$ is understood as arising from the increase in π -bonding interaction afforded by having the sp^2 carbon next to the conjugated chain. Such a preferred location is likely to be a general result for organic semiconductors comprising pi-bonded cores and attached alkyl chains, but further work will be required to verify this conjecture.

Calculations of the migration energy for V_H in the alkyl-chain were performed with a simplified model wherein the chain is attached to a single thiophene ring. The vacancy migrates from carbon number n to $n-1$ by migration of an H atom from $n-1$ to n . An initial state, an intermediate saddle-point structure, and the final state are shown in Fig. 8. Calculations show that the energy of the saddle-point configuration exceeds the energy of the initial state by 1.4 eV. This result for the activation energy for migration of the V_H along the alkyl chain is probably an overestimate because quantum mechanical tunneling of the proton over short distances is not taken into account.

Calculations were performed for the possible structures obtained by bonding an additional H atom to the conjugated chain. Such defects would arise if H atoms that were knocked out of a nearby alkyl-chain rebonded to a conjugated chain. The most stable configuration is the one shown in Fig. 7, which illustrates a defect where the added H atom is bonded to C atom number 4. This structure will be denoted a CH_2 defect. It is also possible to add the H to C atoms 2, 3, 5 or to the S atom. The relative energies of the 5 possibilities were calculated. The CH_2 defect, with the H on C atom 4 is predicted to be more stable than the other 4 possibilities. The relative energies are $\Delta E(5) = 0.33$ eV, $\Delta E(2) = 0.35$ eV, $\Delta E(3) = 0.31$ eV, and $\Delta E(S) = 1.35$ eV. The last value shows that it is highly unlikely that an S-H defect forms.

Migration of H along the conjugated P3HT backbone may occur along a path connecting 2-3-4-5. Calculations indicate that the energy required for H migration along the backbone is ~ 1.2 eV. A saddle point configuration between sites 2 and 5 is shown in Figure 9. In addition it is possible for a CH_2 defect to migrate from one polymer chain to a neighbor. The activation energy for this process was found to be 0.7 eV, and the saddle point geometry, where the H atom is midway between the two polymers is shown in Figure 10. The low activation energy implies that hydrogen can migrate well away from the original molecule.

Given the calculated values for the migration energy it is likely that defects created by x-ray irradiation can be annealed out by recombination of an H atom migrating along the conjugated chain with a V_H that has migrated down the alkyl chain. This model appears to be consistent with the observation of the two different thermal annealing activation

energies. The two activation energies obtained in the experiments are 1.06 eV and 1.14 eV. The calculated migration energy barriers are 1.2 eV and 1.4 eV.

The calculated energy required to create a pair of defects, one CH₂ defect on site 4 of one polymer together with a V_H(A1) on a second polymer, is 2.2 eV. This is significantly less than the expected cost in energy to break a C-H bond (~4 eV). Thus, if the C-H bond breaking occurs concurrently with bond forming it may be possible to create defects in a process requiring less than 4 eV.

Calculations of the electronic structure for P3AT polymer chains containing one CH₂ defect or one V_H defect in each supercell show clearly the presence of localized states in the band gap for both defects. Contour plots of the gap states for the two defects are shown in Fig. 11. The wave-function for the gap state arising from the V_H defect is localized mainly on the sp² bonded C atom in the alkyl chain, but also couples to the C and S atoms in the conjugated chain. The wave-function for the gap state associated with the CH₂ defect is localized near the defect and decays to zero over a distance of about three thiophene rings. The single particle energy level for the V_H defect calculated with LDA is E_{vbm} + 0.22 eV, where E_{vbm} is the energy of the valence band maximum. The corresponding level for the CH₂ defect is E_{vbm} + 0.55 eV. These energy levels were obtained by modeling the defects in ordered P3AT polymers where the tilt angle of the conjugated backbone is equal to 23° and the inter-polymer π-stacking spacing is 3.8 Å.

[1] R. A. Street, J. E. Northrup and B. Krusor, *Radiation induced recombination centers in organic solar cells*, Physical Review B **85**, 165207 (2012).

[2] R. A. Street, J. E. Northrup and A. Krakaris, *The identification of recombination centers in organic solar cells* Tech Connect World 2012; 2012 June 18-21; Santa Clara, CA.

[3] R. A. Street, J. E. Northrup, A. Krakaris and D. Davies *Origin of light-induced degradation in organic solar cells*, oral presentation at MRS Fall 2012, Boston, MA.

Archival publications

- [1] J. Rivnay, L.H. Jimison, J. E. Northrup, M. F. Toney, R. Noriega, S. Lu, T. J. Marks, A. Facchetti, and A. Salleo, *Large modulation of carrier transport by grain-boundary molecular packing and microstructure in organic semiconductors*, Nature Materials **8**, 952 (2009).
- [2] J. E. Northrup, *Two-dimensional deformation potential model of mobility in small molecule organic semiconductors*, Appl. Phys. Lett. **99**, 062111 (2011).
- [3] J. Rivnay, R. Noriega, J. E. Northrup, R. J. Kline, M. F. Toney, and A. Salleo, *Structural origin of gap states in semicrystalline polymers and the implications for charge transport*, Phys. Rev. B **83**, 121306 (2011).
- [4] R. A. Street, K. W. Song, J. E. Northrup and S. Cowan, *Photoconductivity measurements of the electronic structure of organic solar cells*, Physical Review B **83**, 165207 (2011).
- [5] Weiyu Xie, Y. Y. Sun, S. B. Zhang, and J. E. Northrup, *Structure and sources of disorder in poly(3-hexylthiophene) crystals investigated by density functional calculations with van der Waals interactions*, Phys. Rev. B **83**, 184117 (2011).
- [6] R. A. Street, J. E. Northrup and B. Krusor, *Radiation induced recombination centers in organic solar cells*, Physical Review B **85**, 165207 (2012).

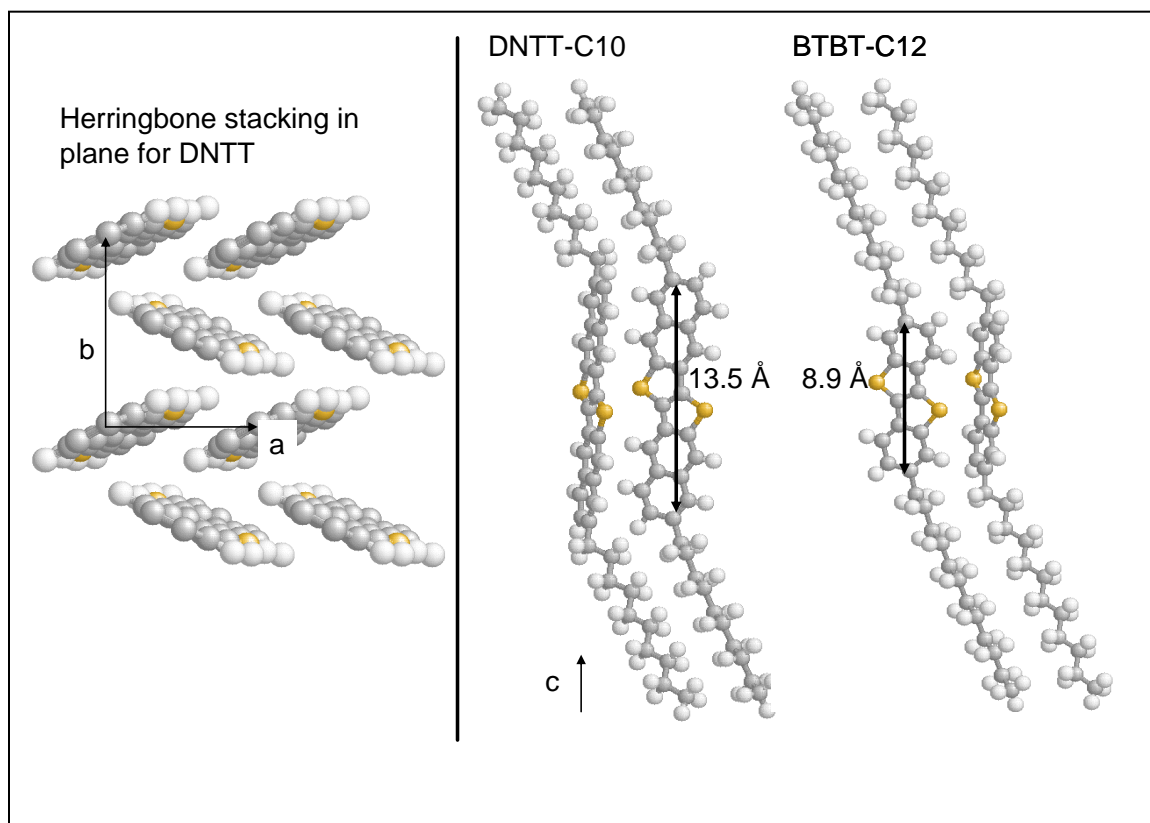


Figure 1. The left panel shows the herringbone stacking for DNTT. Alkyl side chains are omitted here for ease of viewing. The lattice vectors **a** and **b** of the crystal are indicated. The right panel shows DNTT-C10 and BTBT-C12. The lattice vector **c** is perpendicular to **a** and **b**. Calculations of mobility were performed for these systems. The atomic positions were determined by starting with unit cell information obtained experimentally and optimizing the coordinates by first principles density functional theory.

Two dimensional model of mobility appropriate for organic semiconductors

$$\mu = e\hbar^3 B L_{\text{eff}} / [(k_B T) D^2 m_{\text{dos}} m_{\text{con}}]$$

μ = mobility

m_{dos} = density of states effective mass = $(m_a m_b)^{1/2}$

m_{con} = effective mass along direction of transport in x-y plane

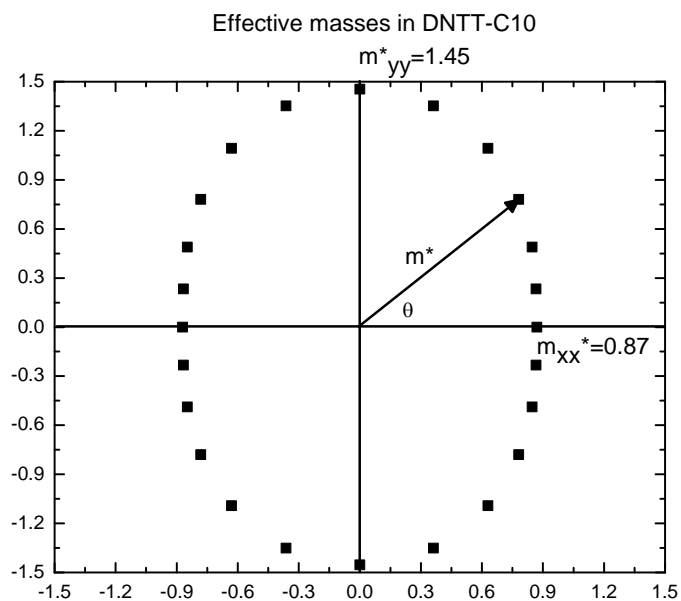
B = elastic constant

D = acoustic deformation potential

L_{eff} measures extent of wavefunction in third dimension (z)

$$(L_{\text{eff}})^{-1} = \int |\psi(z)|^4 dz$$

Figure 2. In the acoustic deformation potential model the mobility depends on the effective masses, the deformation potential and the elastic constant corresponding to compression or expansion of the 2D unit cell area. L_{eff} is the extent of the HOMO wavefunction in the direction perpendicular to transport and is approximately equal to the width of the pi-bonded ring structure in this direction. (These widths are approximately 13 Å for DNTT and 9 Å for BTBT as shown in Figure 1.) This model is appropriate for calculating the mobility for semiconductors in which the transport occurs primarily in two dimensions.



Masses for DNTT-C₁₀

$$m_a = 0.87 \text{ m}$$

$$m_b = 1.45 \text{ m}$$

$$m_{\text{dos}} = (m_a m_b)^{1/2} = 1.12 \text{ m}$$

For comparison:

masses in thin film pentacene:

$$m_a = 2.0 \text{ m}$$

$$m_b = 3.1 \text{ m}$$

$$m_{\text{dos}} = 2.5 \text{ m}$$

Figure 3. The polar plot shows how the effective mass of DNTT-C₁₀ depends on direction. Along the x direction (the **a** direction) the mass is 0.87 m. Along the y direction (i.e. the **b** direction) the effective mass is 1.45 m. Transport is faster along the **a** direction than along any other direction. For transport at a 45° angle to the **a** direction the mass is approximately $\{(0.80\text{m})^2 + (0.85\text{m})^2\}^{1/2} = 1.17 \text{ m}$. Note that the masses for DNTT-C₁₀ are much less than those obtained for pentacene.

Summary of results for three materials

Material	DNTT-C ₁₀	BTBT-C ₁₂	Pentacene
m_a/m	0.87	1.16	3.1
m_b/m	1.45	1.39	2.1
m_{dos}/m	1.12	1.27	2.6
D(eV)	2.2	2.1	1.4
B (eV/Å ³)	0.096	0.108	0.098
W (Å)	13.5	8.9	12.1
μ_a (cm ² /Vs)	96	50	13
μ_b (cm ² /Vs)	58	41	19

Figure 4. The 2D acoustic deformation potential model suggests that the upper limit on room temperature mobility within a single crystalline region in DNTT-C10 or BTBT-C12 may be in the range from 40 to 90 cm² Vs. These values are higher than what has been achieved so far in actual transistors, but are comparable in magnitude to values reported for single crystal rubrene, where mobility has been reported to be ~10 to ~ 40 cm²/Vs. (e.g. Podzorov *et al*, and Takeya *et al*) Subsequent to these calculations it was reported that solution processed BTBT-C8 exhibited mobility of ~15 cm²/Vs (average) and ~30 cm²/Vs (maximum). *Inkjet printing of single-crystal films*, H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas, R. Chiba, R. Kumai, and T. Hasegawa, Nature **475**, 364–367.

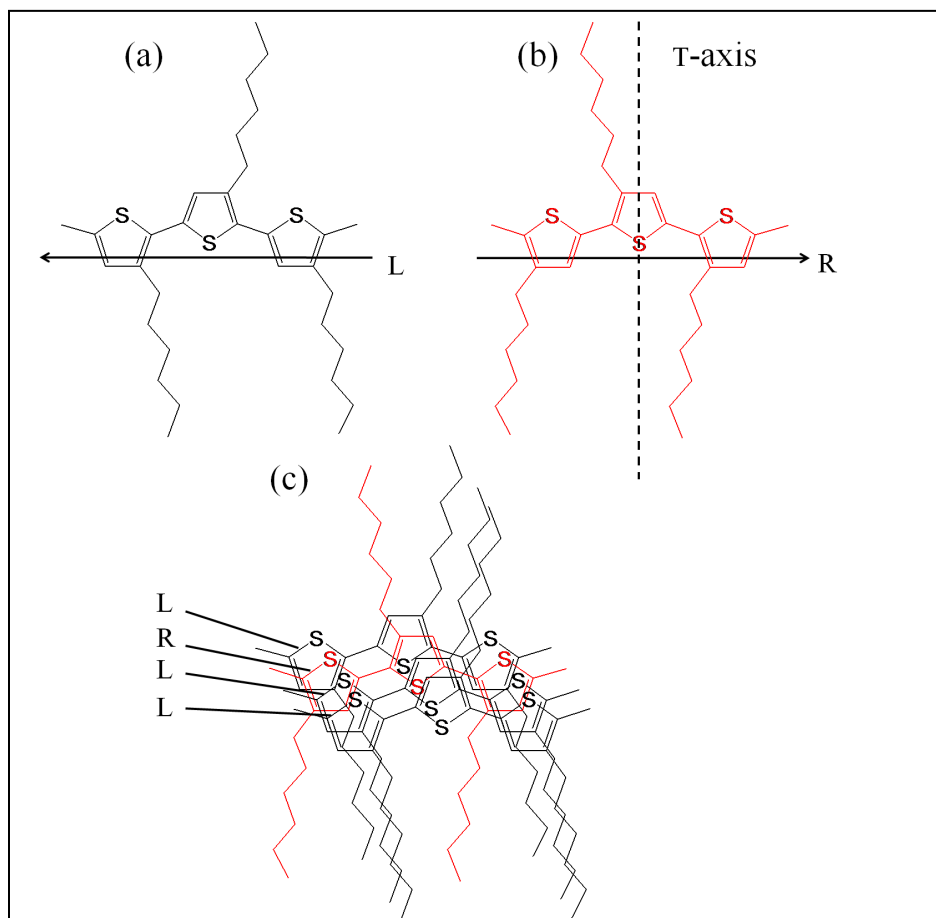


Figure 5. Regioregular head-to-tail alkyl-substituted polythiophene. (a) and (b) are schematic representations of structures defining the L (a) and R (b) backbone chains. L can be converted into R by a 180° rotation around the T axis. (c) This depicts a stacking fault, where an R chain has been inserted into a lamella consisting of L chains. Such defects could form in the process of self-assembly out of solution and could be an important source of structural disorder. A P3HT chain that folds back on its self will contain these defects.

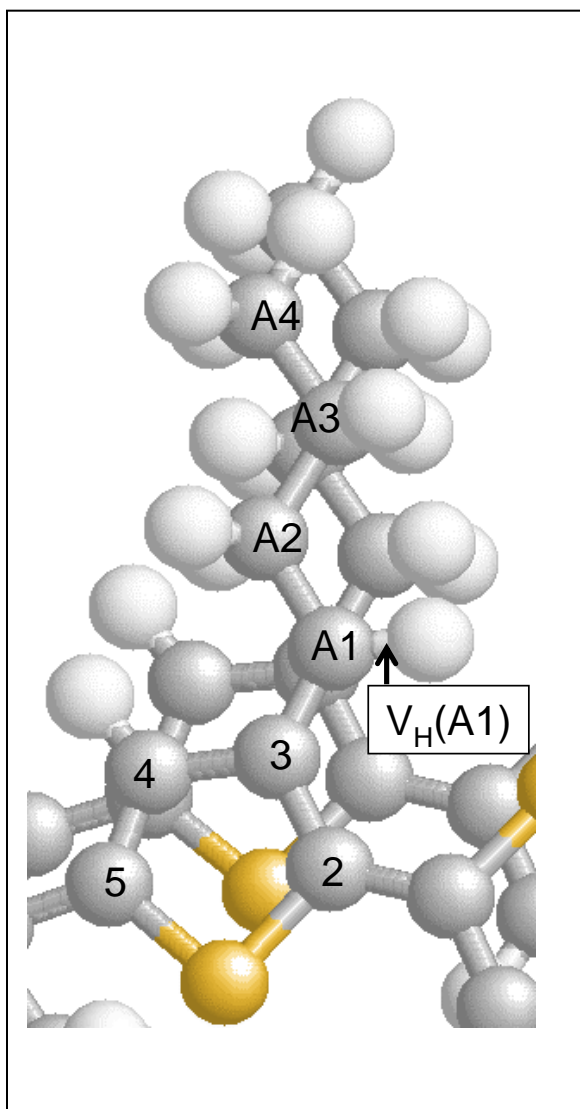
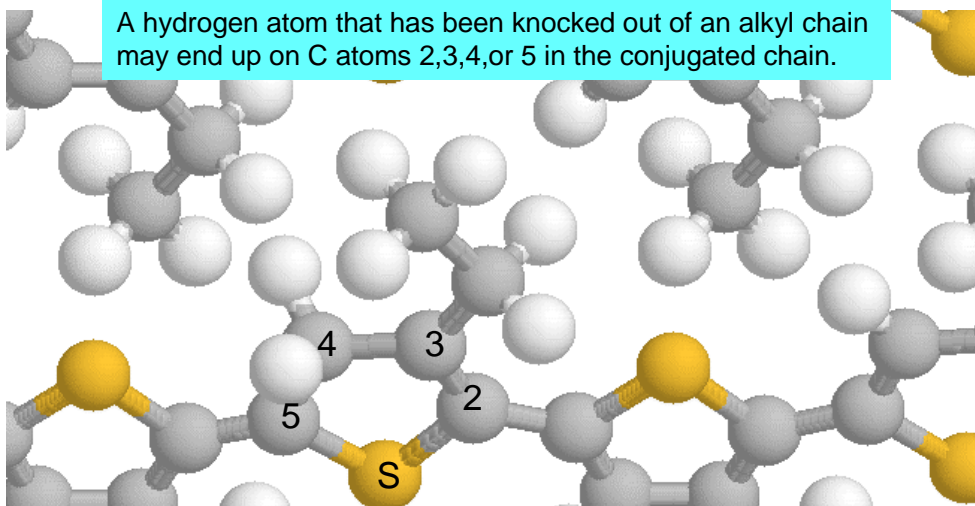


Figure 6. This figure illustrates a defect in which one of the H atoms on the alkyl chain is missing. We refer to such a missing H as a hydrogen vacancy V_H . In this case the V_H is located on the C atom A1, the C atom in the alkyl chain that is nearest to the conjugated chain. This defect $V_H(A1)$ is likely to result from radiation for several reasons. First, our calculations show that $V_H(A1)$ is lower in energy than $V_H(A_n)$ where $n = 2, 3, 4, \dots, N$. Second, the electronic excitations responsible for breaking C-H bonds are more likely to be located on the conjugated chain than on the alkyl chain. So, forming $VH(A1)$ is more likely than forming $VH(A_n)$ because of kinetic factors as well as energetic considerations.

A hydrogen atom that has been knocked out of an alkyl chain may end up on C atoms 2,3,4,or 5 in the conjugated chain.



In this case the extra H atom is on site 4. This may be called a CH₂ defect on site 4.

Figure 7. Shown above is a defect formed by adding a H atom to a thiophene ring. In this case the extra H is attached to C atom number 4. The H may be added on any of the 4 C atoms in the ring or on the S atom. First-principles calculations show that site 4 is preferred over sites 2,3,5 by about 0.3 eV. Addition on the S atom is the highest in energy. It is higher in energy than addition on site 4 by 1.3 eV. Addition on sites 2,3,4,5 gives rise to gap states.

V_H migrates along alkyl chain with an activation energy of 1.4 eV

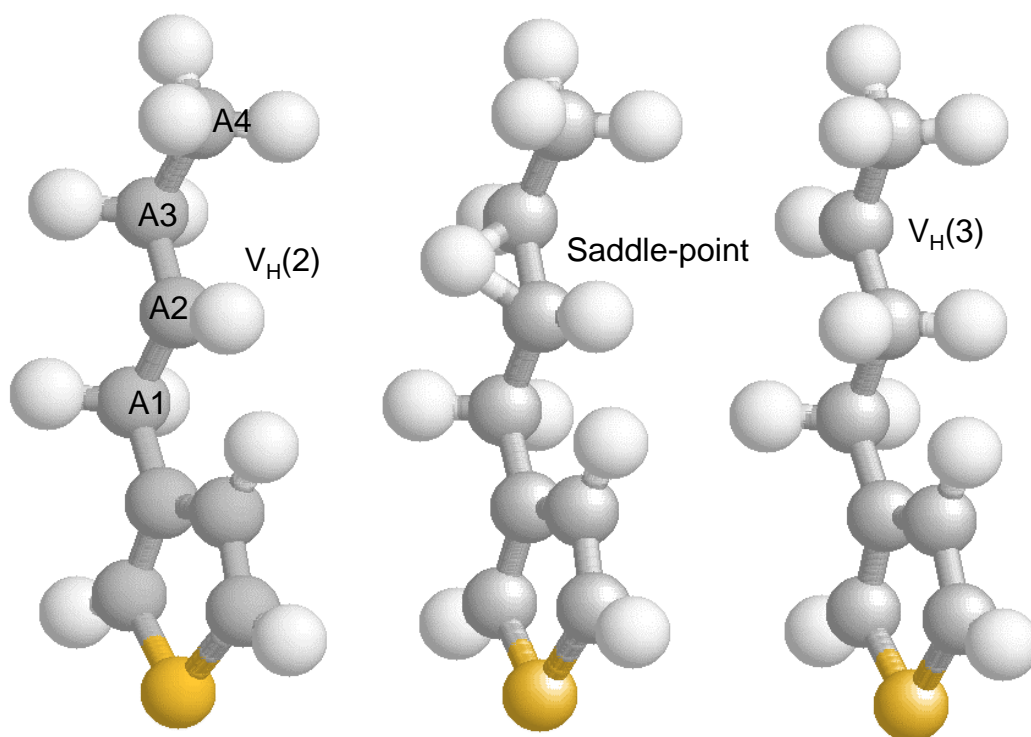


Figure 8. This figure illustrates the migration of the hydrogen vacancy along the alkyl chain, from atom A2 to atom A3. On the left the hydrogen vacancy is located on A2, $V_H(2)$. In the middle frame a hydrogen atom is located in a saddle point. On the right the hydrogen vacancy is located on atom 3, $V_H(3)$. The energy cost to move the H atom to the saddle point is 1.4 eV. This is the migration energy for hydrogen vacancies in the alkyl chain. Vacancies will prefer to reside on atom A1 because of the increased pi-bonding afforded by this configuration.

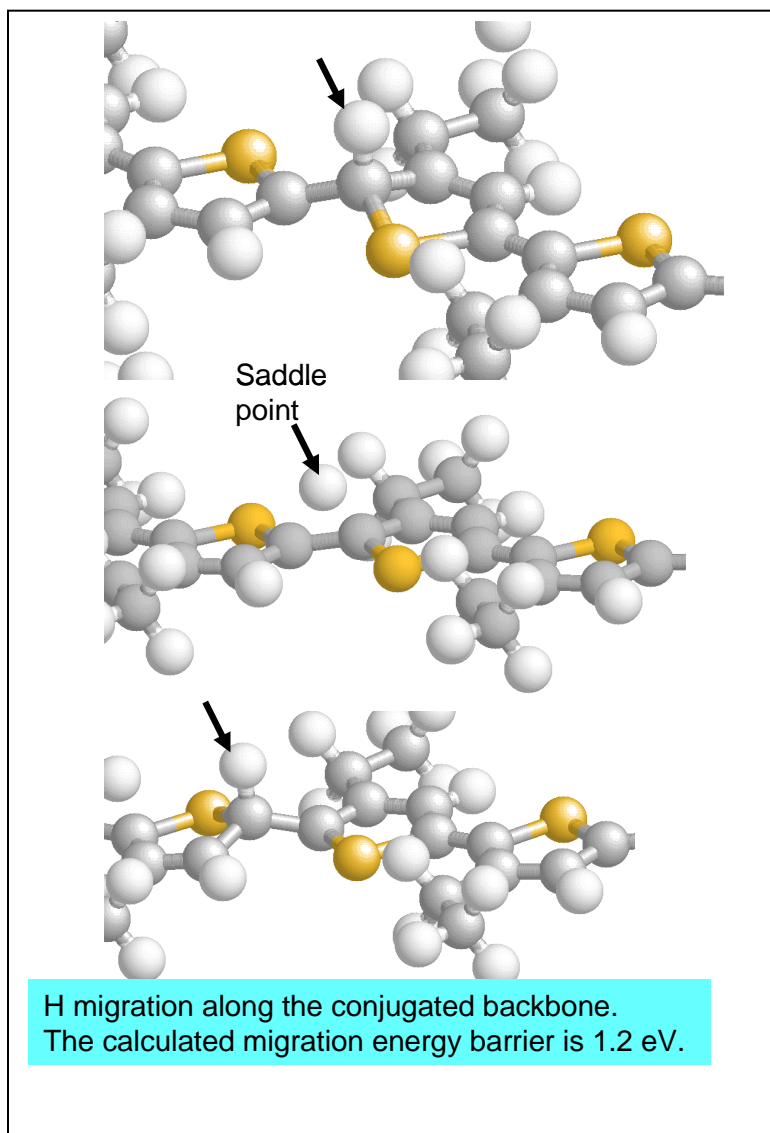


Figure 9. This figure shows part of the path for migration of a H atom along the conjugated backbone. First principles calculations show that the migration energy barrier is 1.2 eV. This value is similar to the activation energy for annealing out the gap states that is measured experimentally.

Hydrogen can migrate from one polymer to another, staying in the same lamella.

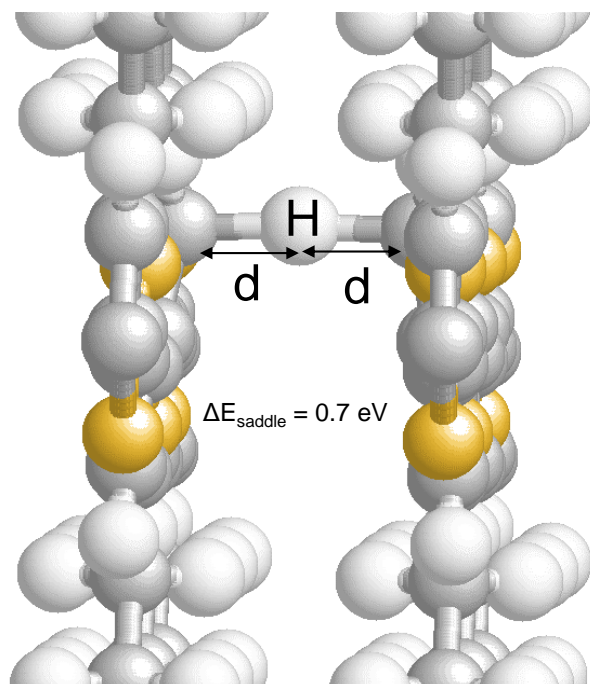


Figure 10. This figure shows a path for a H atom to migrate from one polymer chain to a neighboring chain, staying in the same lamella. According to the calculations the migration of hydrogen between two P3AT polymers occurs with the relatively low activation energy of 0.7 eV. Shown above is a saddle point structure in which the migrating H atom is one-half the way between the two polymers. At the saddle point the C atoms are displaced away from the plane of the polymer by about 0.46 Å, and the C-H distance is stretched to $d = 1.44 \text{ Å}$ from the usual value of $d = 1.1 \text{ Å}$. CH_2 defects can migrate well away from the polythiophene chain where they were created by the irradiation.

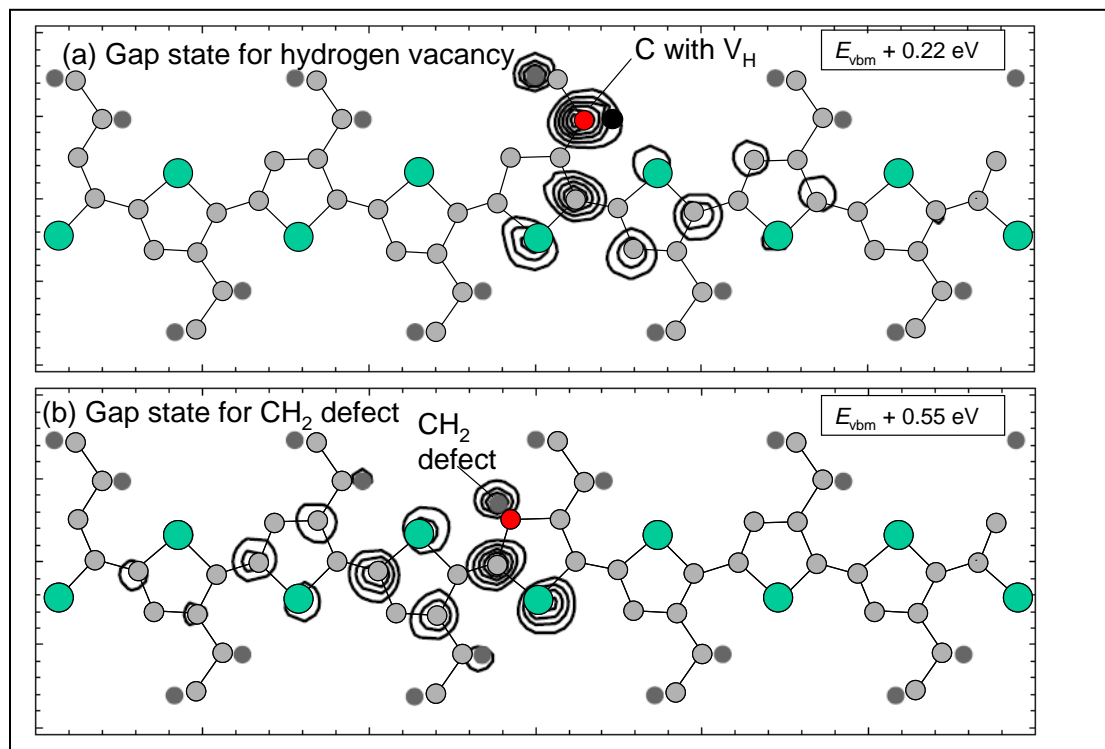


Figure 11. This figure shows contour plots of gap state wave functions for two types of defects. In panel (a) the state corresponds to a hydrogen vacancy on the alkyl chain. In panel (b) the state corresponds to a CH_2 defect on the conjugated chain. These defects may be responsible for degradation effects in polymer organic semiconductors. In each case the wave function is localized near the defect as expected for gap states.